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TI Alloy of solder preventing generation of oxide under fusion - comprises **tin** and/or lead and at least one of **silver**, bismuth, antimony, **indium**, **zinc** and cadmium and **germanium**.
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AB JP62230493 A UPAB: 930922
Solder alloy comprises **Sn**, and/or Pb and contains at least one of **Ag**, Bi, Sb, In, **Zn** and Cd, in which **Ge** in an amt. of 0.001-0.1 (0.00)-0.05) wt.% has been added.
USE/ADVANTAGE - Generation of oxide under fusion is prevented. The alloys have modified solderability.

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SPECIFICATION

1. Title of the Invention Soldering alloy

2. Claim

1. A soldering alloy in which germanium is added by from 0.0001 to 0.1 % by weight in an alloy comprising Sn and/or Pb as the main ingredient and an alloy containing at least one of Ag, Bi, Sb, In, Zn and Cd therein.

2. A soldering alloy as defined in claim 1, wherein germanium is added by from 0.001 to 0.05% by weight.

3. Detailed Description of the Invention

The present invention concerns a soldering alloy with reduced formation of oxides upon melting of solder and improved for solderability (wettability, separability and repellency) by adding germanium (Ge) in Sb or Pb or Sn-Pb series solder and an alloy containing at least one metals such as Ag, Bi, Sb, In, Zn and Cd therein.

Generally, solder is used in a molten state in most cases upon assembling electronic instruments, manufacture of parts,

manufacture of car radiators and electric accessories. In this case, since the molten soldering alloy reacts with oxygen (O_2) contained in air or in molten solder to form a great amount of oxides (MeO), it causes many problems with a view point of manufacturing technique and economical property. Particularly, this tends to occur remarkably in a jetting type soldering bath utilized for soldering printed substrates upon assembling electronic equipments, to bring about problems such as loss of the soldering material due to formation of oxides, and failed products caused by involvement of formed oxides into a jet flow portion.

On the other hand, as the size and the weight have been reduced for electronic equipments in recent years, products have been miniaturized more and more and the demand for the reduction of cost has been increased with an economical point of view, so that interest has been increased more and more in a highly reliable solder corresponding to substrates mounted at high density and low melting solder corresponding to reduction of heat resistant temperature of parts.

As a countermeasure for the formation of oxides in a jetting type automatic soldering apparatus at present, waxes comprising a blend of oils and fats such as mineral oils and vegetable oils and a reducing agent have been used as an anti-oxidant. However, when they are caused to flow on the surface of the molten solder in the jetting bath, no sufficient

effect can be expected in a falling portion of a jetting stream (water fall basin) where oxides are formed most remarkably in view of the physical property of the antioxidant and, further, formation of oxides is prevented by merely shielding a portion of the surface from air also in other portions. In addition, since most of the antioxidants comprise organic compounds, they are denatured to bring about undesirable phenomena of carbonization, decomposition, fuming and increase of viscosity under the effect of heat in the soldering bath thereby remarkably contaminating the soldering bath to lower the working efficiency, being coupled with involvement of formed oxides to the jetting stream portion. Further, while the use of a phosphorus (P)-incorporated alloy material has been proposed with the same purpose as that of the present invention (JP54-84817A, JP54-128459A), since the P content added is consumed by selective oxidation in the molten alloy, the time for retaining the anti-oxidation effect is in proportion with the addition amount of P. Accordingly, a considerable amount of P has to be added in order to maintain the anti-oxidant effect for a long period of time. However, since addition of excess P gives undesired effects on the property of the solder such as roughening, repellency and poor wettability, the upper limit for the concentration of P has to be kept to about 0.01 wt%. Therefore, when the phosphorus-containing alloy is used, it is necessary to control the concentration of the phosphorus

under a high temperature of 300°C or higher, it also shows excellent characteristic compared with phosphorus-containing alloy also for the use at high temperature. Further, since Ge is a metal similar with Sn and Pb, electrical migration less occurs in the soldered portion different from the case of P, and the migration is rather smaller when compared with that of solder with no additive. Furthermore, a prominent feature obtained by the addition of Ge lies in the improvement for the solderability of the soldering alloy. As a trend of electronic industry in recent years, it has been demanded for miniaturization of products by reducing the weight and decreasing the size of the products, and reduction of the cost due to use of IC(s) and improvement of parts, and this naturally leads to the demand for the development of solder having high reliability and solder of low melting point.

Usually, development for the highly reliable solder or low melting solder have been conducted by using the method of blending Sn or Pb or a mixture thereof with metal elements such as Ag, Bi, Sb, In, Zn and Cd, thereby forming a polynary alloy. However, depending on the type and the amount of the additive elements, it may possibly cause additional defects. For instance, the melting point of the low melting solder shown in Example 3 is lowered by the addition of Bi (135 - 165°C), but soldering characteristics such as wettability, spreadability and separability are inferior to Sn-Pb series solders. However,

if Ge is added to the alloy, the soldering property is improved and a low melting and highly reliable soldering alloy as an aimed object of the invention can be obtained by the improvement of the solderability. Further, when Ge is added to several kinds of Sn-Pb series binary alloys, improvement for the solderability can be seen in comparison with alloys with no additives, and similar results can be obtained also by the addition to other polynary alloys.

That is, addition of a small amount of germanium as the feature of the present invention not only suppresses the amount of oxides formed during melting of the soldering alloy but also shows remarkable contribution to the reliability of the solder such as improvement in the solderability of the Ge-added alloy, namely, improvement in the wettability and the separability to the matrix metal and suppression of icicles and bridges causing soldering failure as compared with solder with no additives.

Further, when it is used as a raw material for powdery cream solder as an application example of the present invention, it shows an effect of preventing occurrence of a so-called solder ball and improving the soldering reliability due to the reduced thickness of oxide layers on the powder surface.

In order to obtain the effect of suppressing the occurrence of oxides and improving the soldering property by the addition and incorporation of Ge in the alloy comprising Sn and/or Pb and the alloy containing at least one of Ag, Bi, In, Zn and Cd

therein, it is necessary to incorporate Ge at least by 0.0001 wt% in the alloy. If Ge is incorporated by more than 0.1 wt%, the cost of the alloy is increased by the use of expensive Ge in a great amount, which is not practical. Ge is preferably contained by 0.001 to 0.05 wt% in the alloy.

Examples are shown below.

Example 1

For alloys comprising 60% Sn (H60A*) solder and alloys incorporating Ge therein by 0.0001 wt%, 0.001 wt%, 0.005 wt%, 0.01 wt%, 0.05 wt% and 0.1 wt% respectively, amount of oxides formed, wetting time, separation time, tensile strength upon separation were measured (* JIS H 3282). The results are shown in Table 1.

The method of each of measuring tests were as below.

Amount of oxides formed:

1.5 kg of a soldering alloy is melted in a soldering bath with a surface area of 45.4 cm^2, a rotary type squeezer is attached to the surface, and the weight of oxides formed is measured after one hour.

Wetting time, separation time, tensile strength upon separation:

Measured under the following conditions by using a meniscographic method.

Solder melting temperature: 250°C

Flux: VV 35% IPA solution of gum rosin, produced in USA

Test piece: 2.0ϕ x 30 mm Cu wire

Test instrument: Solder checker SAT-2000 type (manufactured by Resuka)

Table 1

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyr/cm)
H60A	31.8	7.06	1.71	134.2
+ 0.0001 Ge	26.2	7.00	1.70	134.0
+ 0.001 Ge	20.2	6.92	1.62	122.0
+ 0.005 Ge	17.6	6.00	1.56	101.4
+ 0.01 Ge	15.9	5.79	1.52	95.3
+ 0.05 Ge	14.9	5.51	1.47	91.8
+ 0.1 Ge	14.1	5.44	1.45	90.5

Example 2

35% Sn (H35A) solder and alloys incorporating Ge by the same ratios as those in Example 1 were measured in the same manner as in Example 1 except for increasing the melting temperature to 300°C. The results are shown in Table 2.

Table 2

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyr/cm)
H35A	40.3	7.23	1.85	122.8
+ 0.0001 Ge	38.7	7.21	1.78	110.0
+ 0.001 Ge	30.2	6.81	1.66	99.5
+ 0.005 Ge	21.9	6.22	1.61	95.8
+ 0.01 Ge	20.5	6.07	1.57	94.1
+ 0.05 Ge	19.7	5.93	1.56	92.7
+ 0.1 Ge	18.5	5.81	1.54	91.4

Example 3

A low melting solder comprising a blend of 43Sn-43Pb-16Bi and alloys with addition of Ge by the same ratios as those in Example 1 were measured in the same procedures as those in Example 1 excepting for lowering the melting temperature to 200°C. The results are shown in Table 3.

Table 3

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyr/cm)
Sn-Pb-Bi	46.3	7.44	1.28	38.7
+ 0.0001 Ge	45.8	7.44	1.27	38.7
+ 0.001 Ge	25.9	7.07	1.18	32.9
+ 0.005 Ge	22.8	6.84	1.13	30.6
+ 0.01 Ge	20.8	6.25	1.12	29.0
+ 0.05 Ge	18.5	6.10	1.10	27.5
+ 0.1 Ge	17.1	5.95	1.04	27.1

Example 4

An automatic jetting type solder bath of 300 kg capacity (Model FS-300, manufactured by Nippon Dennetsu Keiki) was used and the amounts of oxides formed for 63% Sn (H63A) solder and alloys with addition of 0.005 wt% of Ge at 250°C were compared (time) and shown in Fig. 1.

4. Brief Explanation of the Drawings

Fig. 1 is a view showing a relationship between the time and the index of oxides formed in the example for H63A and an alloy incorporating therein 0.005 wt% of Ge as the example of the present invention.

Fig. 1

(1) Amount of oxide formed (kg)

(2) Example of the Invention

(3) Time (hrs)

Amendment

Dated April 30, 1986

6. Content of Amendment

(1) In Table 1, Table 2 and Table 3, on page 9 and page 10:

correct the unit for the tensile strength upon separation: from "(dyr/cm)" into "(dyn/cm)".

(2) In line 4, page 11:

correct "index of oxides formed" into "amount of oxide formed"

Amendment

Dated June 30, 1987

6. Content of Amendment

(1) Insert the following sentence between lines 4 and 5 on page 7 of the specification.

"Further, while the soldering property described above has been considered to have high dependency on to the working temperature (solder bath temperature) so far, but the addition of germanium (Ge) proposed by the present invention shows an effect of lowering the operation temperature by 5 to 30°C for all of the combined alloys described in the scope of the claim for patent by the addition of germanium (Ge) proposed by the present invention. In other words, as apparent from the table for Example 1, addition of germanium shows similar solderability at a lower temperature as compared with a case of using a soldering alloy with no additives at 250°C.

The above mentioned feature resides in the provision of an effect of lowering the working temperature upon soldering electronic instruments without changing the combination of soldering alloys and with no change of property corresponding thereto and it shows a possibility of eliminating disadvantages caused upon lowering the melting point of solders described previously.

Furthermore, the above mentioned feature can provide

similar effects not only for tin (Sn), lead (Pb) series solder as shown in Example 1 but also for bismuth (Bi) added alloy shown in Example 3 and, further, also to a polynary alloy with addition of one or several kinds of metals such as bismuth (Bi), silver (Ag), antimony (Sb), indium (In), zinc (Zn) and cadmium (Cd) into the Sn-Pb series alloy.

This is because the addition of germanium, different from the existent polynary alloys, improves the surface tension of the alloy as a base, the interfacial tension between the soldered matrix or flux and flowability of molten soldering alloy is improved."

(2) Amend Table 1 on page 9 of the specification as below.

" Table 1

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyn/cm)	Working temperature * (°C)
H60A	31.8	7.06	1.71	134.2	(250)
+ 0.0001 Ge	26.2	7.00	1.70	134.0	245
+ 0.001 Ge	20.2	6.92	1.62	122.0	238
+ 0.005 Ge	17.6	6.00	1.56	101.4	232
+ 0.01 Ge	15.9	5.79	1.52	95.3	230
+ 0.05 Ge	14.9	5.51	1.47	91.8	225
+ 0.1 Ge	14.1	5.44	1.45	90.5	223

* Working temperature (soldering bath temperature) required for obtaining a performance identical with that of alloys with no Ge additive at the specified temperature."

(3) Amend Table 2 on page 9 of the specification as below.

"

Table 2

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyn/cm)	Working temperature * (°C)
H35A	40.3	7.23	1.85	122.8	(300)
+ 0.0001 Ge	38.7	7.21	1.78	110.0	295
+ 0.001 Ge	30.2	6.81	1.66	99.5	290
+ 0.005 Ge	21.9	6.22	1.61	95.8	288
+ 0.01 Ge	20.5	6.07	1.57	94.1	285
+ 0.05 Ge	19.7	5.93	1.56	92.7	280
+ 0.1 Ge	18.5	5.81	1.54	91.4	278

* Working temperature (soldering bath temperature) required for obtaining a performance identical with that of alloys with no Ge additive at the specified temperature."

(4) Amend Table 3 on page 10 of the specification as below.

"

Table 3

	Oxide formed per 1 hr (gr)	Wetting time (sec)	Separation time (sec)	Separation tensile strength (dyn/cm)	Working temperature * (°C)
Sn-Pb-Bi	46.3	7.44	1.28	38.7	(200)
+ 0.0001 Ge	45.8	7.44	1.27	38.7	198
+ 0.001 Ge	25.9	7.07	1.18	32.9	195
+ 0.005 Ge	22.8	6.84	1.13	30.6	190
+ 0.01 Ge	20.8	6.25	1.12	29.0	185
+ 0.05 Ge	18.5	6.10	1.10	27.5	183
+ 0.1 Ge	17.1	5.95	1.04	27.1	180

* Working temperature (soldering bath temperature) required for obtaining a performance identical with that of alloys with no Ge additive at the specified temperature."